

Modeling of Ground-Water Contamination Caused by Organic Solvent Vapors

by Carl A. Mendoza^a and Todd A. McAlary^b

Abstract

Mathematical models are used to evaluate the potential for ground-water contamination resulting from vapor transport of volatile organic solvents in the unsaturated zone. A two-dimensional numerical model for density-driven flow and transport of vapors shows that trichloroethylene (TCE) vapors can be expected to spread rapidly from a residual source above an unconfined aquifer in an unsaturated, sandy deposit. Sensitivity analyses show that the shape of the vapor plume is particularly sensitive to the ground surface boundary condition and the material permeability. The shape of the vapor plume is insensitive to the mass flux by diffusion through the capillary fringe, although the flux may be significant in terms of ground-water quality because the drinking-water standard is very low. The vapor plume simulations and a plug-flow infiltration model are used to calculate a source function for a ground-water transport model in order to estimate the potential for ground-water contamination. Ground-water simulations show that an impermeable surface cover could reduce the flux of contaminants to the aquifer by preventing infiltration through the vapor plume. However, for the conditions modeled, significant ground-water contamination can be expected to occur regardless of whether the ground surface is covered or not. Contaminants can reach the saturated zone from a residual source either by liquid-phase diffusion through the capillary fringe or by migrating as a vapor beyond the lateral limits of a cover and subsequently dissolving and being flushed to the saturated zone by infiltration.

Introduction

Vapor transport in the unsaturated zone has an important influence on the fate of volatile organic compounds released into the subsurface. Schwille (1988) suggested that vapors from solvents may spread laterally by diffusion and density-driven advection in the unsaturated zone and lead to ground-water contamination; however, there are few quantitative analyses of the problem presented in the literature. An understanding of the transport processes involved is important for the determination of the extent of contamination and for the design of remedial measures.

Discrete solvent releases in the subsurface move primarily downward through the unsaturated zone, leaving behind a trail of liquid solvent which occupies a small fraction of the pore space. Although this residual solvent is immobilized by capillary forces, the contaminant may reach the saturated zone by dissolving in the soil moisture and being transported by infiltration, liquid-phase diffusion, or a fluctuating water table. Since infiltration is generally the most important of these processes, it is common practice in remedial programs to place an impermeable cover on the ground surface over the residual solvent to minimize ground-water contamination. Many hydrophobic organic solvents, however, will vaporize readily and migrate through the gas phase in the unsaturated zone, which constitutes an alternative pathway to the saturated zone. Dissolution of the vapors in the soil moisture creates an

effective source of ground-water contamination which can spread so quickly that the liquid residual itself is soon insignificant by comparison (Sleep and Sykes, 1989). In these cases, a surface cover over the residual solvent alone may not provide adequate protection from ground-water contamination.

The objective of this study was to simulate the ground-water contamination resulting from vapor transport, dissolution, and infiltration for a hypothetical case where a residual solvent source occurs above the water table in a sandy unconfined aquifer. A two-dimensional finite-element model was used to simulate vapor transport of trichloroethylene (TCE) from a residual source in the unsaturated zone and to conduct sensitivity analyses for the influence of the ground surface and water-table boundary conditions and the permeability of the geologic material. The results of the unsaturated zone model were used to define a source for a ground-water transport model to evaluate the potential for ground-water contamination from spreading solvent vapors. The models were used collectively to simulate the effect of placing a low-permeability cover over a solvent spill site in an attempt to diminish the severity of ground-water contamination.

The rationale for choosing TCE as the compound was that it is one of the most common organic contaminants found in ground water. Since many other chlorinated solvents have properties similar to those of TCE, the general results of the study apply to many cases where volatile chlorinated solvents are accidentally released into the unsaturated zone.

The approach of using decoupled models for the unsaturated and saturated zones was chosen to give an acceptable balance between the accurate representation of the physical processes and the appropriate level of mathematical complexity justified for the hypothetical scenario being considered. Decoupling results in more efficient models since the spatial and temporal scales of transport in

^aWaterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

^bBeak Consultants Limited, 14 Abacus Road, Brampton, Ontario, Canada L6T 5B7.

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the two zones are different. One-dimensional transport models have been developed by Weeks *et al.* (1982) and Baehr and Corapcioglu (1987); however, two dimensions are required to represent the lateral spreading of the vapors. The two-dimensional models of Abriola and Pinder (1985) and Baehr (1987) do not consider advection in the gaseous phase, and so were not suitable for this study since density-driven advection may be important for chlorinated solvents. The model developed by Sleep and Sykes (1989), which considers advection and dispersion in both the gaseous and aqueous phases, was not available at the time of this study. Thus, a new model, based partly on that of Allan (1986), was developed to simulate the transport of vapors in the unsaturated zone. Existing flow and transport models were used for the saturated zone.

Mass Transport Modeling in Porous Media

The mathematical simulation of subsurface contaminant plumes is obtained by solving the partial differential flow and transport equations, subject to boundary and initial conditions. The general mathematical equations describing fluid and mass transport in granular materials are applicable to both the gaseous and aqueous phases (Bear, 1972). In this study, transport in the saturated and unsaturated zones was simulated separately since gaseous phase transport is restricted to the unsaturated zone and we assumed that aqueous phase transport dominates only in the saturated zone.

Some general assumptions were made which apply to the governing equations for both fluid phases. Chemical and biological transformations were not considered, so the results are restricted to compounds that are not degraded over the time scales of the simulations. The gas, liquid, and solid phases were all assumed to be essentially incompressible and under isothermal conditions. The temperature was chosen to be 20°C. Additional assumptions are discussed later.

Flow and Transport in the Unsaturated Zone

In the unsaturated zone, gas flow may result from pressure gradients or density gradients within the vapor plume. Pressure gradients due to vacuum extraction were not considered in this study and the effects of barometric pressure fluctuations were assumed to be negligible. Density gradients were considered as a function of molecular weight and vapor concentration relative to natural soil gas. Density flow can be modeled using the same mathematical formulation as for the density-dependent ground-water flow model presented by Frind (1982). To maintain numerical efficiency, an equivalent head (h^*) and relative density (ρ_r) may be defined:

$$h^* = \frac{P}{\rho_a g} + z \quad \rho_r = \frac{\rho}{\rho_a} - 1 \quad (1a, b)$$

where ρ is the density of the gas mixture, ρ_a is the density of uncontaminated air, P is the fluid pressure, and g is the gravitational constant.

In the absence of large pressure gradients, the gas phase may be assumed incompressible, and density is then a function of concentration only (Sleep and Sykes, 1989).

The two-dimensional flow equation for the vapor phase is then:

$$\frac{\partial}{\partial x} \left\{ k_x^* \frac{\rho_a g}{\mu} \frac{\partial h^*}{\partial x} \right\} + \frac{\partial}{\partial z} \left\{ k_z^* \frac{\rho_a g}{\mu} \left(\frac{\partial h^*}{\partial z} + \rho_r \right) \right\} = S_s \frac{\partial h^*}{\partial t} \quad (2)$$

where k_x^* and k_z^* are the principal directions of effective permeability (assumed to be horizontal and vertical), and μ is the gas mixture viscosity. In this study, the effective gas permeability is taken as being 80% of the intrinsic permeability. The specific storage is defined by:

$$S_s = \theta_g \rho_a g \gamma \quad (3)$$

where γ is the macroscopic compressibility of the gas phase, and θ_g is the gas-filled porosity.

The unsaturated zone transport equation developed here ignores transport in the aqueous phase by assuming that the soil moisture is held motionless by capillary tension. This is reasonable if infiltration, evapotranspiration, and water-table fluctuations are negligible over the period of time represented by the vapor transport simulation. The vapor transport equation for static moisture conditions may be written as:

$$\frac{\partial}{\partial x} \left\{ \theta_g \left(D_{xx} \frac{\partial c}{\partial x} + D_{xz} \frac{\partial c}{\partial z} \right) \right\} + \frac{\partial}{\partial z} \left\{ \theta_g \left(D_{zx} \frac{\partial c}{\partial x} + D_{zz} \frac{\partial c}{\partial z} \right) \right\} - v_x \frac{\partial}{\partial x} (\theta_g c) - v_z \frac{\partial}{\partial z} (\theta_g c) = \frac{\partial}{\partial t} (\theta_g R_v c) \quad (4)$$

where c is the concentration, and v_x and v_z are the velocities. The vapor dispersion tensor is:

$$D_{ij} = \alpha_T |v| \delta_{ij} + (\alpha_L - \alpha_T) \frac{v_i v_j}{|v|} + D_a^* \delta_{ij} \quad (i, j = x, z) \quad (5)$$

with α_L and α_T being the longitudinal and transverse dispersivities, respectively, and δ_{ij} is the Kronecker delta.

For nonreactive vapors in moist granular soils, Millington and Quirk (1961) showed that the effective diffusion coefficient (D_a^*) can be calculated from the free-air diffusion coefficient (D_a) using the relationship:

$$D_a^* = \frac{\theta_g^{7/3}}{\theta_t^2} D_a \quad (6)$$

where θ_t is the total porosity.

The effects of sorption and dissolution reactions can be accounted for by using a vapor retardation factor of the form suggested by Weeks *et al.* (1982). The retardation factor for the vapor phase is then:

$$R_v = 1 + \frac{\theta_w}{\theta_g} K_h + \frac{\rho_b}{\theta_g} K_h K_d \quad (7)$$

where K_h is the inverse dimensionless Henry's Law constant (mg/l liquid per mg/l gas), K_d is the solid-liquid partitioning coefficient (mg/g solid per mg/ml liquid), ρ_b is the bulk density of the soil, and θ_w is the water-filled porosity. The first term in (7) accounts for mass removed by dissolution into the soil moisture assuming two-phase equilibrium described by Henry's Law; the second term accounts for sorption onto the solids from the aqueous phase assuming a linear sorption isotherm. These phase transfer reactions are

assumed to be essentially instantaneous. This formulation is not valid for very dry soils where sorption increases dramatically and becomes strongly nonlinear (Chiou and Shoup, 1985), nor for highly advection-dominated situations where reaction kinetics should be considered (Johnson *et al.*, 1987). The geologic setting used here is expected to satisfy the above constraints, but more research is needed to determine the range of conditions under which these assumptions are valid.

Flow and Transport in the Saturated Zone

Ground-water flow was simulated at steady-state by neglecting temporal flow variations and the effects of the solvent on the physical properties of the aqueous solution. The solubility of TCE in water is low enough for the second assumption to be valid. In terms of hydraulic head (h), the two-dimensional steady-state flow equation for water in the saturated zone is:

$$\frac{\partial}{\partial x} \left(K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial h}{\partial z} \right) = 0 \quad (8)$$

where K_x and K_z represent the principal directions of hydraulic conductivity.

For saturated transport, the advection-dispersion equation is:

$$\begin{aligned} \frac{\partial}{\partial x} \left(D_{xx} \frac{\partial c}{\partial x} + D_{xz} \frac{\partial c}{\partial z} \right) + \frac{\partial}{\partial z} \left(D_{zx} \frac{\partial c}{\partial x} + D_{zz} \frac{\partial c}{\partial z} \right) \\ - q_x \frac{\partial c}{\partial x} - q_z \frac{\partial c}{\partial z} = \theta_w R_d \frac{\partial c}{\partial t} \end{aligned} \quad (9)$$

where R_d is the retardation factor for dissolved solutes, and q_x and q_z are the Darcy fluxes. The aqueous dispersion term is defined as:

$$D_{ij} = \alpha_T |q| \delta_{ij} + (\alpha_L - \alpha_T) \frac{q_i q_j}{|q|} + D_w^* \delta_{ij} \quad (i, j = x, z) \quad (10)$$

where D_w^* is the effective aqueous diffusion coefficient.

Boundary and Initial Conditions in the Unsaturated Zone

The upper and lower boundary conditions for the unsaturated domain were modeled using theoretical methods of estimation for the boundary mass transfer coefficients. Since these estimation methods have not been verified experimentally, a sensitivity analysis was conducted for each boundary condition. The ground surface boundary was simulated as: (1) an impermeable boundary intended to represent a building foundation, pavement, or frozen ground, or (2) a permeable boundary with vegetative cover. The impermeable boundary was simulated by specifying zero gradients of head and concentration normal to the boundary. The permeable boundary was simulated using the boundary layer theory of Thibodeaux (1981). If a stagnant layer of air of thickness h_{gs} exists above the ground surface, the steady-state diffusive flux across the layer can be described by:

$$\theta_g D_n \frac{\partial c}{\partial n} - \theta_g v_n c = \frac{D_a}{h_{gs}} c_{gs} \quad (11)$$

where c_{gs} is the vapor concentration at the ground surface boundary, D_n is the normal dispersion coefficient within the domain, v_n is the normal velocity within the domain, and n is the unit normal to the boundary. The concentration in the atmosphere is assumed to be zero. The head along the permeable boundary was constrained to correspond to constant atmospheric pressure.

The top of the saturated zone has been assumed to be impermeable to transport in most previous vapor models; however, a diffusive flux must be considered if a concentration gradient exists between the unsaturated and saturated zones. Assuming that the rate limiting mass transfer process is aqueous phase diffusion through a horizontal flow layer of thickness h_{wt} near the capillary fringe, the steady-state boundary flux can be described by an equation similar to that used by Weeks *et al.* (1982):

$$D_n \frac{\partial c}{\partial n} = \frac{D_w^*}{h_{wt}} c_{wt} \quad (12)$$

where c_{wt} is the aqueous phase concentration at the top of the boundary layer. The concentration at the bottom of this boundary layer is assumed to be zero. Since this boundary is impermeable to gas flow, the head gradient was specified to be zero.

The initial condition for flow was a static air phase everywhere. For transport, zero concentration was specified everywhere but the source.

Numerical Method of Solution

The Galerkin finite-element method was applied using triangular elements and linear basis functions. Details of the method were presented by Wang and Anderson (1982) and Huyakorn and Pinder (1983). The vapor flow equation was solved using implicit time-weighting, while the vapor and aqueous transport equations were solved using the Crank-Nicolson time-weighting scheme. Stability and accuracy problems were controlled by satisfying the Peclet and Courant criteria (Daus *et al.*, 1985).

In the vapor model, the flow and transport equations are not independent because the velocities from equation (2) are required for the solution of equation (4), yet the velocities depend on the concentrations calculated from (4). An iterative solution was used therefore to solve repeatedly the flow and transport equations until the concentrations converged to within 0.001% of the source concentration between iterations. With TCE as the solvent, only two iterations were generally necessary, except at early times where three to five iterations were required because of high-density gradients.

Output from the vapor model was compared to simple linear analytical solutions of the diffusion and advection-dispersion equations to verify that the basic equations were being solved correctly. The conservation of mass was shown to be acceptable by mass balance calculations, which compared the mass input to the domain, to the difference between the mass stored within the domain and the mass transported across the boundaries. Experimental data that definitively exhibit density-driven advection do not yet exist (Sleep and Sykes, 1989), so the model could not be rigorously validated.

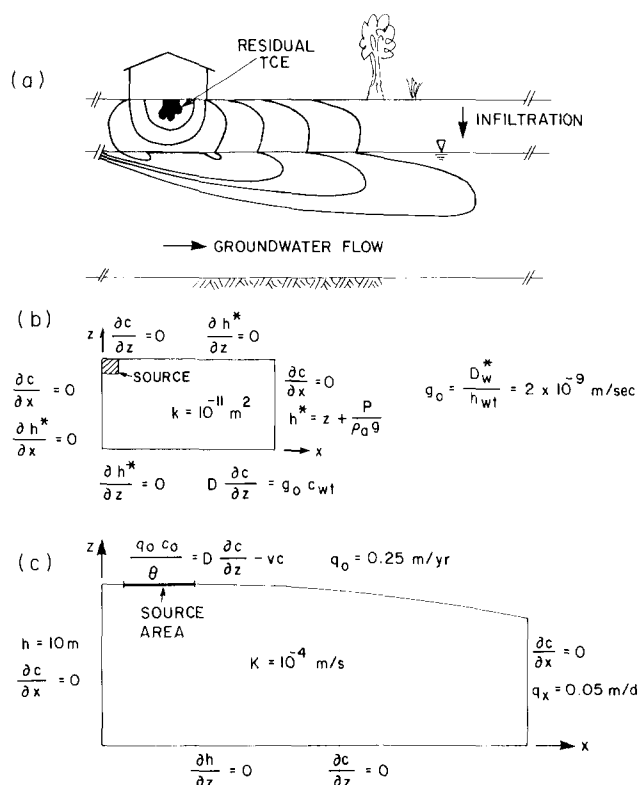


Fig. 1. (a) Schematic representation of hypothetical setting. Domain and boundary conditions for (b) the unsaturated zone base case, and (c) the saturated zone.

The ground-water flow equation was solved using a potential/stream function model (FLONETS) based on the dual formulation of flow (Frind and Matanga, 1985). Only a single solution of the flow equation was required for each simulation because the ground-water flow was assumed to be at steady-state. The transport equation was then solved using a general purpose solute transport model (FEMTRAN). These models, developed by E. O. Frind and E. A. Sudicky at the University of Waterloo, have been tested extensively and applied to a number of situations.

Physical Setting

The vapor and ground-water models were applied to a hypothetical geologic setting in a humid, temperate climatic region intended to be representative of south-central Canada or the northeastern United States. Although the models will accommodate heterogeneity and anisotropy, a simple setting of an unconfined aquifer in a homogeneous, isotropic, medium-grained, sandy deposit was considered sufficient to show the potential impact of vapor plumes on ground-water quality. A schematic representation of the setting, with postulated vapor and ground-water plumes, is shown in Figure 1 along with the domains and boundary conditions for the simulations. The physical properties for both domains are summarized in Table 1.

The soil moisture content throughout the unsaturated zone was assumed to be uniform at a field capacity of 6% of bulk volume. In reality, there is a transition zone of gradually increasing moisture contents above the saturated zone, but this was ignored here to avoid extremely small elements near the capillary fringe. Increased moisture

contents near the bottom of the unsaturated zone would be expected to reduce vapor transport rates and increase mass partitioning to the aqueous phase.

The source of organic vapors was assumed to originate from a hypothetical surface spill of 200 l (approximately one barrel) of trichloroethylene (TCE) which spread out uniformly over a 1 m by 3 m area and infiltrated until it reached residual saturation. Assuming that the residual saturation was uniform at 15% of the pore volume, which is within the range reported by Schwille (1988) for medium sand, the residual liquid solvent would penetrate to a depth of 1.2 m. We assume that vaporization was fast enough so that the local soil gas was continually saturated with TCE vapors, and thus the vapor source would have a constant concentration of 7.9% (by volume) and a relative density (compared to air) of 1.3. The coexisting aqueous phase at equilibrium would be saturated with TCE at a concentration of about 1100 mg/l.

Results of Unsaturated Zone Modeling

The results of the vapor model are shown as plots of one-half of the unsaturated domain because of the symmetry about the residual solvent source. The fate of TCE was calculated for the half domain and is summarized in Table 2 for each of the vapor simulations. Mass balance errors were less than 0.01% of the vaporized mass.

The contours in Figures 2, 3, and 4 show the vapor concentration expressed as a fraction of the source vapor concentration (430 mg/l gas). From Henry's Law and the assumption of equilibrium between the gas and liquid phases, the vapor contours correspond to aqueous concen-

Table 1. Simulation Parameters

Unsaturated zone (base case)	
Effective permeability, k^*	$8.0 \times 10^{-12} \text{ m}^2$
Bulk-water content, θ_w	6%
Porosity, θ_t	30%
Bulk density, ρ_b	1.65 g/ml
Effective diffusion coefficient, D_a^*	$3.2 \times 10^{-6} \text{ m}^2/\text{s}$
Longitudinal dispersivity, α_L	1.0 m
Transverse dispersivity, α_T	0.1 m
Inverse Henry's constant, K_h	2.56
Partitioning coefficient, K_d	0.01 ml/g
Calculated retardation factor, R_v	1.8
Water-table diffusion thickness, h_{wt}	0.3 m
Domain dimensions	4 by 24 m
Domain discretization	11 by 31 nodes 600 elements
Saturated zone	
Hydraulic conductivity, K	$1.0 \times 10^{-4} \text{ m/s}$
Porosity, θ_t	30%
Effective diffusion coefficient, D_w^*	$3.0 \times 10^{-10} \text{ m}^2/\text{s}$
Longitudinal dispersivity, α_L	2.0 m
Transverse dispersivity, α_T	0.1 m
Assumed retardation factor, R_d	1.0
Domain dimensions	10 by 224 m
Domain discretization	21 by 71 nodes 2800 elements
Both zones	
Temperature, T	20°C

trations in the soil moisture as a fraction of the solubility. Although the drinking-water standard for TCE is about five orders of magnitude lower than the solubility, only the first three orders of magnitude are shown on the plots since numerical dispersion may cause significant errors at lower levels.

Base Case

The base case simulation shows the vapor plume development for the medium-grained sand deposit described in the previous section. It is intended to be used as a basis for comparing the results of the sensitivity analyses. It was also used to generate the source function for the ground-water zone modeling.

The base case vapor plume after 45, 90, and 135 days is shown in Figure 2. The shape of the base case plume is very similar to simulations conducted using a zero density gradient (see Figure 4) which indicates that diffusion is the dominant transport mechanism. The effect of density-driven advection is barely detectable, but it results in the contours extending slightly further from the source near the bottom of the domain. Again, it should be noted that vapor migration just above the water table would be expected to be slower than shown because of the increased retardation with increasing moisture content that was not accounted for in the simulations.

The base case simulations indicate that vapor transport can cause rapid spreading of contaminants from a residual solvent source in unsaturated sand. The source of potential ground-water contamination expands with the vapor plume since the vapors will dissolve into the local soil moisture and can be transported later to the saturated zone by aqueous-phase diffusion, infiltration, or a fluctuating water table.

Sensitivity Analysis

1. Ground Surface Boundary

The sensitivity analysis on the ground surface boundary condition shows the effect of natural venting to the atmosphere. The shape of the vapor plume after 135 days is shown in Figure 3 for the cases of an impermeable ground surface cover, a permeable ground surface with a thick boundary layer ($h_{gs} = 1$ m), and a permeable ground surface with a thinner boundary layer ($h_{gs} = 0.25$ m). The thickness of the boundary layer of air above the ground surface corresponds to about two-thirds the height of the vegetative cover (Oke, 1978). For each of the permeable cases, the ground surface was modeled as being impermeable to a distance of 6 m from the source to show the effects of passive venting at the edge of a cover.

Both of the permeable ground surface simulations show that venting to the atmosphere can be an important attenuation mechanism for vapor plumes, although the effect diminishes with depth below the surface. An impermeable surface cover minimizes natural venting, thereby maximizing the areal extent of the effective source of ground-water contamination. Vapors will eventually spread beyond the limits of a surface cover where infiltration can transport dissolved contaminants to the water table, thereby counteracting the remedial effects of the surface cover.

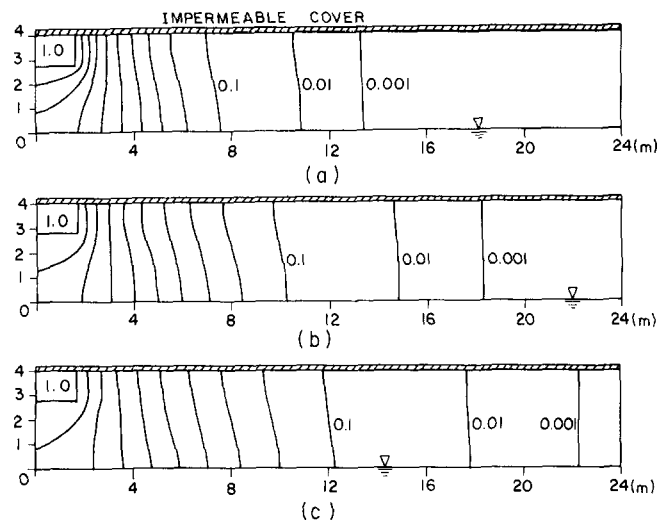


Fig. 2. Base case TCE vapor plume development: (a) 45, (b) 90, and (c) 135 days. Contours represent vapor concentrations relative to the source vapor concentration, or equivalently, soil moisture concentrations relative to saturation.

This study did not consider some factors which may affect the ground surface boundary flux. Barometric pressure fluctuations might increase vertical dispersion near the ground surface resulting in increased venting of TCE to the atmosphere. A rising water table would also increase venting to the atmosphere. Organic-rich soil layers near the ground surface would decrease venting through an increase in sorption. Similarly, sorption onto mineral surfaces has been shown to increase dramatically at very low moisture contents which can occur near the ground surface (Chiou and Shoup, 1985).

2. Water-Table Boundary

A sensitivity analysis on the water-table boundary condition was conducted to determine the effect of diffusion

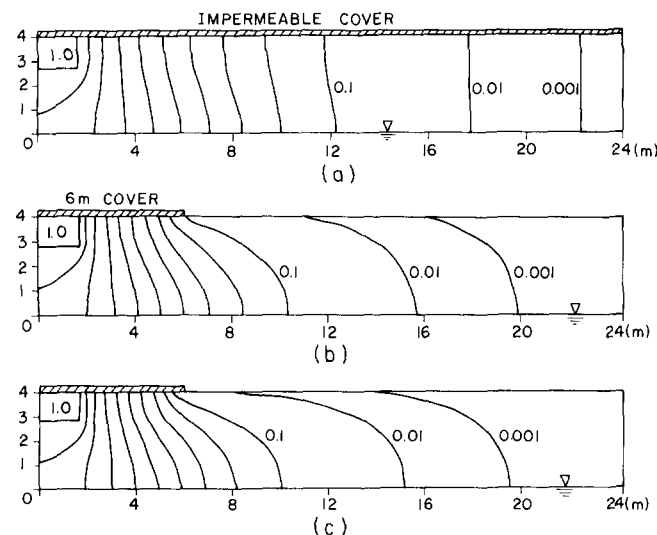


Fig. 3. Effect of the ground surface boundary condition on TCE vapor plumes after 135 days: (a) impermeable surface (base case), (b) a thick boundary layer ($h_{gs} = 1.0$ m), and (c) a thinner boundary layer ($h_{gs} = 0.25$ m).

Table 2. Mass Fate for Vapor Transport Simulations

Simulation	Source vaporization (kg)	Vapor phase (kg)	Retarded phase (kg)	Atmospheric losses (kg)	Water-table losses (g)
Base case:					
90 days	4.02	2.23	1.79	0.00	2.68
135 days	4.79	2.66	2.13	0.00	5.09
Ground surface sensitivity (135 days):					
$h_{gs} = 1.0$ m	5.05	2.12	1.70	1.24	4.76
$h_{gs} = 0.25$ m	5.15	2.03	1.62	1.50	4.68
Water-table sensitivity (135 days):					
$h_{wt} = 3.0$ m	4.79	2.66	2.13	0.00	0.509
$h_{wt} = 0.03$ m	4.81	2.56	2.12	0.00	50.5
Permeability sensitivity (90 days):					
Diffusion only	3.47	1.98	1.59	0.00	2.03
$k^* = 8 \times 10^{-11}$ m ²	7.55	4.19	3.35	0.00	7.34

Values are for the half domain, 1-m wide in the third dimension.

into the saturated zone. Vapor transport simulations were conducted with three different mass transfer coefficients which correspond to boundary layer thicknesses (h_{wt}) of 3, 30, and 300 cm. In all cases, the mass flux across the water table was small enough to have a negligible effect on the shape of the vapor plume; however, it might have a considerably more important effect on ground-water quality. The mass fate values in Table 2 confirm that there was little effect on the vapor plume, but the mass transported into the saturated zone by diffusion alone was between 0.5 and 50 g for the half domain after 135 days. This may be a considerable load since the U.S. EPA drinking-water standard for TCE is 5 $\mu\text{g/l}$. Ground-water contamination may therefore occur even in the absence of infiltration or water-table fluctuations. Thus, the water table should not be considered an impermeable boundary for contaminant transport from solvent vapors if ground-water contamination is the primary concern.

3. Material Permeability

The sensitivity analysis of material permeability shows the potential effects of density-driven vapor advection. The vapor plumes after 90 days are shown in Figure 4 for a pure diffusion case with density gradients removed, the base case, and a high-permeability case with an order of magnitude increase in permeability relative to the base case. The high-permeability material is equivalent to a clean coarse sand (aqueous hydraulic conductivity, $K = 10^{-3}$ m/s), whereas the material of the base case is equivalent to a clean medium sand ($K = 10^{-4}$ m/s).

Based on the similarity between the base case and the pure diffusion simulations, it is evident that molecular diffusion is the dominant vapor transport mechanism for TCE in a medium sand deposit. Advection becomes increasingly important as the permeability increases, although diffusion still dominates near the periphery of the vapor plume because the density gradient diminishes at lower concentrations. For chemicals whose vapor density is significantly different from air, subsurface vapor advection should be considered until it is shown to be negligible for the specific chemical and geological conditions. Models which

neglect advection may underestimate the rate of vapor transport and fail to provide conservative estimates for the protection of ground-water resources.

Results of Saturated Zone Modeling

The saturated zone simulations show the effect of placing an impermeable cover on the ground surface over the residual solvent in an attempt to reduce ground-water contamination by controlling infiltration. In the first case, a 13-m long impermeable cover was placed over the center of the vapor plume, and infiltration was restricted to the uncovered areas. In the second case, the ground surface boundary was completely uncovered.

Ground-Water Flow

The steady-state ground-water flow model was used to calculate the velocities needed to solve the transport equation. The flow model solved iteratively for the position of the water table based on a prescribed head value of 10 m

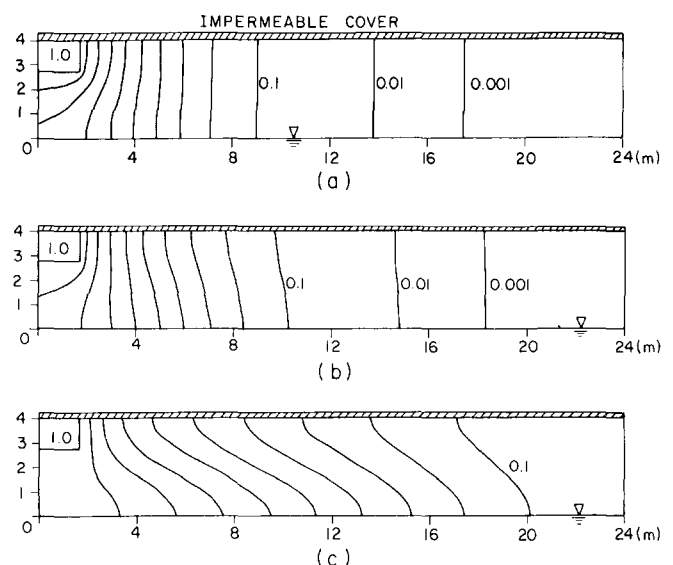


Fig. 4. Effect of density-driven advection on TCE vapor plumes after 90 days: (a) pure diffusion, (b) 8×10^{-12} m² permeability (base case), and (c) 8×10^{-11} m² permeability.

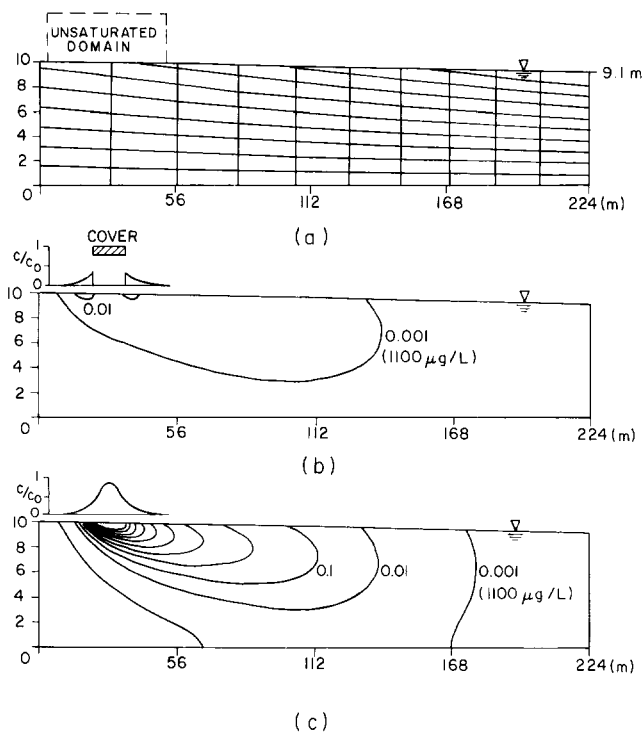


Fig. 5. (a) Saturated zone flownet for the uncovered case showing the location of the model domain for the vapor simulations. TCE ground-water plumes after three years and input concentration functions for (b) the covered case, and (c) the uncovered case. Contours represent aqueous concentrations relative to saturation (1100 mg/l).

on the left boundary and a prescribed Darcy flux of 0.05 m/d on the right boundary. The lower boundary was impermeable. Infiltration was considered constant at 25 cm/yr over the uncovered portions of the upper boundary. For both cases, the resulting horizontal velocities ranged from about 0.08 m/d (30 m/yr) near the left boundary to 0.14 m/d (50 m/yr) near the right boundary, and the elevation of the upper right corner of the domain was 9.12 m. Figure 5(a) shows the flownet for the uncovered case. The covered case flownet was very similar in appearance.

Ground-Water Transport

The input of TCE to the saturated zone was calculated using a simple plug-flow infiltration model. The mass flux was defined by multiplying the infiltration rate by the aqueous TCE concentration at the water table. The diffusive flux through the capillary fringe was considered to be negligible by comparison. For the covered case, the flux beneath the cover was specified to be zero. The aqueous concentration at the water table was selected from the base case vapor simulation at 135 days. The base case scenario was used since the concentration distribution at the water table was not particularly sensitive to the ground surface boundary condition. The time of 135 days was chosen so that the rate of net mass input by vaporization into the unsaturated zone was of the same order as the rate of mass removed by infiltration into the ground-water zone, a condition which would correspond to stabilization of the unsaturated zone plume. Although the actual concentration distribution at the water table changes over time, this

snapshot was considered sufficient to show the effects of controlling infiltration through a vapor plume. The water-table concentration distributions used for each case are shown on Figures 5(b) and 5(c).

Figures 5(b) and 5(c) show the dissolved plumes after three years for the covered and uncovered cases, respectively. Since the contours represent aqueous concentrations relative to saturation, the outermost contour represents a concentration of 1.1 mg/l. This concentration is still several orders of magnitude greater than the U.S. EPA drinking-water standard of 5 μg/l, and thus, the zone of contamination actually extends for some distance beyond this outer contour. Limitations on the accuracy of numerical model simulations prevent a full description of the problem to concentrations as low as the drinking-water standard.

For these three-year simulations, the mass input to the ground-water zone for the uncovered case was 6.15 kg, whereas the input for the covered case was only 0.93 kg. While the extent of ground-water contamination is less severe in the covered case, infiltration beyond the limits of the cover still causes extensive ground-water contamination. Considering the low drinking-water standards for TCE, alternative remedial measures would be required if the aquifer was to be used for a drinking-water supply. Ground surface covers therefore should be considered only as a partial form of remediation for vadose zone solvent spills and should be supplemented with vapor control systems or alternative remedial strategies for maximum effectiveness.

Conclusions

Vapor transport and subsequent dissolution of volatile organics have been shown to be potentially important sources of ground-water contamination. For a spill of TCE in a permeable sandy material, a vapor plume will spread a few tens of meters through the unsaturated zone within a few months by molecular diffusion and possibly by density-driven advection. Phase transfer reactions will contaminate the soil moisture within the vapor plume and significantly increase the size of the potential source of ground-water contamination. The dissolved TCE may be transported to the saturated zone by infiltration, water-table fluctuations, or liquid-phase diffusion across the capillary fringe.

The ground surface boundary condition is a sensitive parameter for vapor transport. A permeable ground surface allows natural venting to the atmosphere which reduces the lateral extent of the unsaturated zone vapor plume; however, it also allows infiltration which can flush contaminated soil moisture into the saturated zone. An impermeable cover over the ground surface will reduce surface venting and increase the lateral migration of the vapor plume.

The water-table boundary should not be considered impermeable to mass transport when investigating the potential for ground-water contamination from solvent vapor plumes. Liquid-phase diffusion can cause a flux of volatile organics across the capillary fringe. The mass flux by diffusion alone is generally too small to affect the shape of the vapor plume; however, it may cause significant contamination in the ground-water zone.

Ground-water simulations demonstrate that a cover at the ground surface can greatly reduce the flux of solvent

mass to the saturated zone by preventing infiltration through the residual source and the concentrated regions of a vapor plume. However, because of infiltration beyond the limits of a surface cover and the low concentrations of concern, the reduction in mass flux does not lead to a comparable reduction in the size of the ground-water plume. Surface covers therefore are not considered to be effective remedial measures for the protection of ground-water quality.

Although the simulations presented here are for TCE, the results generally can be expected to apply to other volatile chlorinated solvents. Similar behavior is expected since many other solvents have high vapor pressures and Henry's constants, which favor vapor phase transport in the unsaturated zone. In addition, small amounts of solvent can contaminate large volumes of ground water to undesirable levels because drinking-water standards are generally very low. For example, 1,1,1-trichloroethane, which has a Henry's constant twice that of TCE, will migrate faster in the unsaturated zone. Dichloromethane has a Henry's constant that is one-quarter that of TCE, so migration will be slower; however, its high solubility will place large amounts of mass in the soil moisture that can then be transported to the ground-water zone.

More research is required in order to more fully understand the processes by which aquifers can become contaminated through vapor transport. In particular, experimental data are necessary to validate the theoretical basis for the density-driven advection of vapors, and additional chemicals and geological settings should be investigated.

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Carl A. Mendoza is a Ph.D. candidate in the Department of Earth Sciences at the University of Waterloo. He has a B.A.Sc. from the University of British Columbia and was formerly employed as a Geological Engineer in the petroleum industry. His M.Sc. research at the University of Waterloo focused on understanding and modeling the transport and fate of organic solvent vapors in the subsurface.

Todd A. McAlary is a Contaminant Hydrogeologist with Beak Consultants Limited. He received his B.A.Sc. in Geological Engineering from the University of Waterloo where he studied the behavior of volatile organics in monitoring piezometers for his Bachelor's thesis. McAlary has an M.Sc. degree in Earth Sciences from Waterloo, having developed an experimental method for measuring effective vapor diffusion coefficients for his Master's project. He is currently involved in several assessment and remediation projects involving volatile solvents.